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Interfacial Synthesis of Electrically Conducting Polyaniline Nanofiber Composites

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14. ABSTRACT

In this work, polyaniline/poly(sulfonated styrene) nanofiber composites were prepared by an interfacial method. The *in-situ* polymerization technique of these PANI nanofibers in the presence of sulfonated polystyrene allowed for the growth of PANI 2-D nanostructures embedded in the polymerized sulfonated host. This facile approach enables a self-assembly of these nanofibers into a workable, robust, conductive composite that can be processed and cast from water. A low accelerating voltage SEM was used to image these twisted fibers within the bulk of the cast film. In addition, the SEM confirmed the self-assembly of these 40–50 nm fibers within the host PSS to yield an electrically conducting composite film.

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1. Introduction

Electrically conducting polymers such as polyaniline (PANI) are viewed as 'organic metals' due to their metallic-like conductivity combined with the processability of organic polymers. The unique non-redox acid/base doping/dedoping chemistry of PANI and its consequence on structural, spectroscopic, and electronic transport properties allows PANI to be versatile in its end properties. It is well known that the design of the dopant not only increases electronic conductivity, but also alters electronic transport, processability, and optical properties. This 'dopant engineering' recently has shown to have consequences on polyaniline's morphology at the nano-scale. The method frequently employed to construct such morphologies has typically involved template-free chemical synthesis in which the aniline monomer polymerizes in the presence of large bulky acids. For instance, Huang et al.[1] recently developed a simple, practical method using a bi-phasic or "interfacial" polymerization for making uniform, template-free nanofibers. Furthermore, Wan et al.[2] developed a template-free solution method in which the diameter of the tube could be controlled by the dopant functionality and amount. Nanostructured polyaniline (nano-tube/wire/fiber/rod) is potentially useful in applications such as sensors and other nano-devices due to the advantages of both organic conductors and one-dimensional nanostructures.

While considerable effort has been expended toward the fabrication of these conducting polymer nanostructures, less attention has been paid in the literature to the processing of these nanofibers. The intractability of these polymer nanostructures, such as the nano/micro-tubes made by *in-situ* doping methods, presents limits to their processability. If polyaniline nanostructures can be made *in-situ* within a more processable host, conceptually it would eliminate the need for post-processing these nanostructures into a blend. This novel fabrication of electrically conducting nanocomposite preserves the integrity of the nanostructures without perturbing the electronic properties of polyaniline and the mechanical properties of the host polymer.

In this work, we have utilized the ability of PANI to form well-defined nanofibers to form a two-dimensional mesh of PANI fibers within an insulating host material. During the template-free interfacial polymerization[1] of these nanofibers, a macromolecular dopant [sulfonated polystyrene (PSS)] was chosen as both the host and dopant. The interfacial technique allows the formation of the nanofibers with diameters well below 100 nm. It is thought that the PSS protonates the aniline to yield anilinium ions, and during this polymerization, the 2-D nanofibers are ionically embedded in the polymerized sulfonated host. During polymerization, the PSS dopes the precipitated polyaniline nanofibers to yield the conducting salt; the resulting polystyrene sulfonate counter-anion also act as an imbedded host that is ionically attracted to the conducting nanofiber. This self-assembly technique allows for *in-situ* processing of these nanostructures in the host material. This facile approach to polymerizing PANI nanocomposites in the presence of sulfonated polystyene is unique in that it yields well-defined 2-D nanofibers, as confirmed by scanning electron microscopy (SEM).

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2. Experimental Details

PANI-PSS nanocomposites were synthesized by the following method: Predistilled aniline was dissolved in CCl_4 (A.C.S. Reagent, Aldrich Chemical) while ammonium peroxydisulfate (98%, Aldrich Chemical) was dissolved in water with 100 mol% poly(sulfonated styrene) (PSS) (Versa-TL 71, Alco Chemical) with a molecular weight of 70,000 g/mol. When transferred to a 200 mL beaker, an interface formed between the two immiscible solutions. Green polyaniline soon formed at the interface, then slowly migrated into the water layer. The entire water phase was finally filled with dark emeraldine green polyaniline polymerized in the presence of PSS. The by-products were removed from the aqueous phase using dialysis.

2.1   Electron Microscopy

Scanning electron microscopy (SEM) was used to examine the polyaniline/poly(sulfonated styrene) (PANI-PSS) nanofiber composite to identify the PANI nanostructured features within the embedded polystyrene. The JEOL 6401-F uses a cold-field emission electron source with a tungsten single-crystal tip. The sample chamber operated at a vacuum of 5.3×10^{-5} Pa. To prevent charging, a low accelerating voltage of 2 kV was used to image the conducting nanofibers. At such low accelerating voltage, it was not necessary to coat the polymer composite with any conducting layer, such as pyrolytic carbon or gold. A tip of less than 6×10^{-13} A allowed images up to 150,000x magnification at 2 kV without charging.

2.2   Electrical Conductivity

The films were deposited on an array of interdigitated gold electrodes on glass substrates fabricated at The Aerospace Corporation. The geometry of the electrodes consisted of 50 pairs of fingers, each finger having a dimension of $20 \times 4970 \times 0.18 \ \mu m^3$ with a 10-μm gap between fingers. The electrode array was mounted in a standard 24-pin dip package and wire bonded via gold contact pads. The resistances were measured with a Keithley 617 electrometer.

3. Results and Discussion

The formation of polyaniline nanofibers in the presence of poly(styrene sulfonic acid) (PSS) is illustrated in Figure 1. It is believed that the PANI nanofibers are formed at the interface where the aniline monomer and PSS meet. In this controlled, interfacial polymerization, the aniline is protonated by the PSS in the presence of the oxidant, ammonium persulfate. During this oxidative polymerization of aniline, the 100 % sulfonated polystyrene (an acidic, strong polyelectrolyte) acts as a proton source for the dopant and provides the necessary counterions to the developing charged polyaniline. In order for the interfacial polymerization to occur, the polyacid dopant must have a pK_a lower than that of the aniline monomer whose pK_a is 4.63. Note that the PSS maintains the water solubility of the final nanofiber composite complex. In this template-free synthesis, it is unclear what driving force(s) are involved in forming these nanofibers; however, it is hypothesized that there may be some preferential electrostatic alignment[3] of the aniline monomer onto the anionic polyelectrolyte dopant
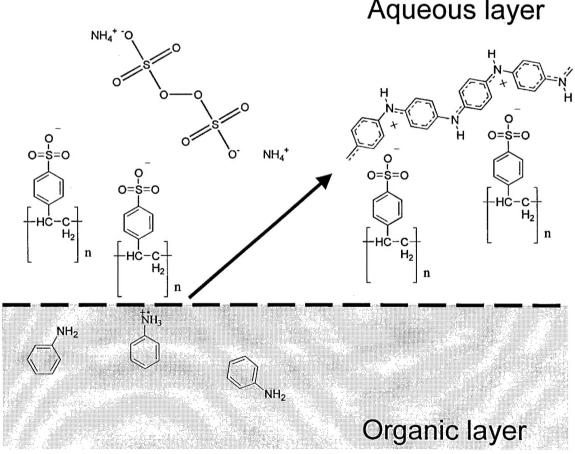

Figure 1.   Snapshot of interfacial polymerization of aniline. The top layer is an aqueous solution of poly(styrene sulfonic acid) and ammonium peroxydisulfate, while the bottom layer contains dissolved aniline in CCl_4.

(i.e., PSS), which is optimized by the interfacial method. Liu, et al.[3] argued that the interface between the immiscible organic/aqueous system acts as a template that preferentially organizes the aniline monomer prior to polymerization. It is thought that as the aniline monomer is protonated on the surface, its head-to-tail coupling forms a low-energy helical structure when polymerized and precipitated into the aqueous phase of the biphasic system.

As the polymerization time increases to 15 min, a dark-green precipitate is seen to form in the top aqueous layer and deepens in both intensity and color after 25 min. The nanofibers imbedded in PSS yield a homogeneous dark-green complex after the by-products are removed. FTIR spectra of the polyaniline/poly(sulfonated styrene) (PANI-PSS) confirm the presence of doped polyaniline in the presence of the PSS host. In the nanofiber composite, benzenoid and quinoid ring vibrations were observed at 1500 cm^{-1} and 1600 cm^{-1}, respectively, confirming the oxidation state of PANI emeraldine salt. In addition, the broad band near 3400 cm^{-1} is assigned to the N-H stretching mode for PANI, while the strong band at 1150 cm^{-1} is an 'electronic-like' band considered to be a measure of the degree of delocalization of the electrons.[6,7] No observed shift of these typical PANI peaks (compared to neat PANI) indicates that the individual components of the composite are preserved; thus, there is no mixing on the molecular level between PANI and PSS.

Although it has been clearly established in the literature[8] that PANI nanotubes or nanofibers with diameters <100 nm can be made, the novelty in this interfacial reaction is the substitution of a conventional doping acid with an acid-functionalized polymer. As seen in Figure 2-a, when camphorsulfonic acid (CSA) is the dopant in an interfacial polymerization route, one can obtain nanofibers with
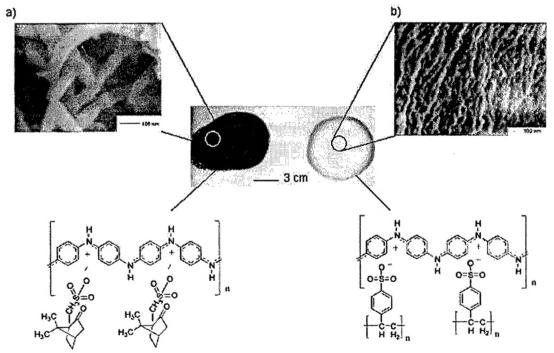

Figure 2.   Optical and scanning electron microscopy (SEM) images of polyaniline nanofibers made by interfacial polymerization using (a) camphorsulfonic acid (CSA) and (b) sulfonated polystyrene (PSS) dopants.

diameters <50 nm. Substituting the molecular dopant, CSA, with a polymer dopant, PSS, the resulting material (Figure 2-b) is a processable, transparent, conductive film. The most important aspect of this procedure is the remarkable self-assembly of these nanofibers within the composite. As seen in the scanning electron microscope (SEM) micrograph in Figure 2, the nanofibers seem to form independent of the dopant functionality, which is consistent with the observations first made by Huang et al.[8]

Individual nanofibers of the PANI-PSS composite were imaged using a microscope that has a low accelerating voltage of 2 kV to avoid charge build-up on the film surface. Figure 3-a is a macro view of the water-cast film that shows gross cracking in the bulk of the film due to very rapid evaporation of water in the vacuum oven. The PANI nanofibers (light color) were not seen on the film surface and were only visible in the bulk of the polymer composite. Probing inside the bulk of the material through the cracks (Figures 3-b, -c, and -d), the SEM reveals 40–50 nm 2-D nanofibers imbedded in the low-emissive polystyrene. The density of the nanofibers appears to be higher in the center of the film and the lengths of these fibers range from 400 nm to a few micrometers. As compared with the neat nanofibers prepared in the presence of a camphorsulfonic acid, the composite nanofibers reveal a twisted surface, which is in contrast to the uniform surface in the PANI-CSA nanofibers (Figure 2-a).

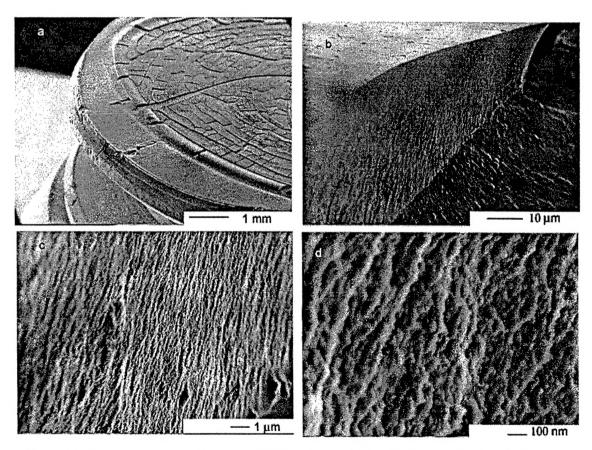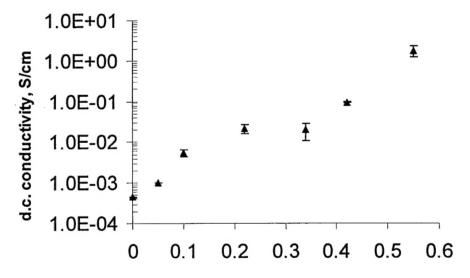Figure 3.   Scanning electron microscope (SEM) images of 40% (wt/wt) polyaniline/poly(sulfonated styrene) (PANI-PSS) nanofiber composite synthesized by interfacial synthesis route: (a) cracked film, (b) view inside a crack, exposing the bulk of the composite film to show (c) and (d) PANI nanofibers (light color) seen in wall of nanocomposite (50 nm in diameter) surrounded by the insulating, low-emissive (dark color) host PSS.

The intimate PSS coating of the aniline nanofiber as it develops in the aqueous phase of the biphasic polymerization is thought to increase the compatibility and stability of the resulting composite. In the nanofiber composite, the individual chains are molecularly wrapped with high molecular weight PSS, which acts to both stabilize the charge carriers on the PANI chains and provides a matrix in which the nanofibers are imbedded. This network ordering is analogous to previously reported blend systems[9] where the connectivity of the conducting PANI salt becomes more ordered due to the crystallization of a host polymer, which yields higher conductivity values versus its amorphous counterpart. However, the ordering in these nanocomposites is not due to the crystallization of the host, but rather the result of a template-free polymerization of the aniline in the presence of the host.

Electrical conductivity has been shown to be sensitive to the morphology of a conducting polymer.[10] To determine the dependence on conductivity of incorporating PSS in the presence of the growing PANI nanofiber, we have examined composites over the composition range of 0–55 % (wt/wt). As shown in Figure 4, PANI-PSS nanocomposites show a gradual increase in conductivity over the increasing PANI weight fraction interval with no sharp indication of a percolation threshold. The absence of a true percolation threshold is indicative of the overpopulation of acid groups compared with the limited number of imine nitrogen sites on the PANI tubes. The abundance of PSS is manifested in its ability to promote molecular compatibility between the two components and also acts to stabilize the electrical conductivity by reducing the doping acid's mobility within the composite. At relatively high concentrations (i.e., 10 %) of imbedded PANI nanofibers, both the optical properties and conductivity are in useful ranges for applications that include electromagnetic shielding and static charge dissipation.

Figure 4.   Electrical dc conductivity as a function of PANI nanofiber con-
centration (wt/wt) in host PSS. Composite concentration range of
0–55 % (wt/wt) loading PANI.

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4. Conclusions

Polyaniline/poly(sulfonated styrene) nanofiber composites have been prepared by an interfacial method. The *in-situ* polymerization technique for the preparation of these PANI nanofibers in the presence of sulfonated polystyrene allows for the growth of PANI 2-D nanostructures. This facile approach enables a self-assembly of these nanofibers into a workable, robust, transparent conductive composite that can be processed and cast from water. The mechanism for this growth is believed to involve some alignment of the aniline monomer onto the anionic dopant, which is optimized by the interfacial method. This method of synthesizing conductive, transparent nanocomposites represents a unique approach utilizing the processability of host polymer and the self-assembly of these 40–50 nm PANI fibers within the composite.

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